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#### Bibliography.

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[Theme code (reference)]

4K030. 5F033.

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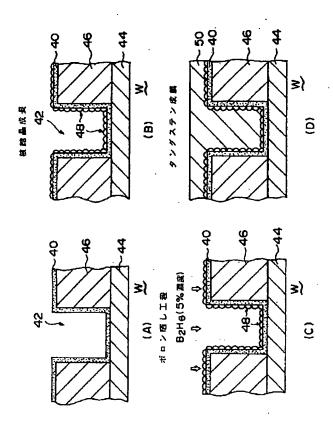
## Summary.

(57) [Abstract]

[Technical problem] The membrane formation method of the tungsten film which can make resistivity

[Means for Solution] It faces forming the tungsten film 50 on the front face of the processed object W in the vacuum processor 2. It constitutes so that it may have the tungsten membrane-formation process which the aforementioned nuclear crystal grows up and forms a tungsten film in the bottom of existence of the membrane-formation gas which includes the aforementioned processed object after the nucleus crystal-growth process of growing up the nuclear crystal 48 of a tungsten into the bottom of existence of the membrane-formation gas containing a tungsten element on the front face of the aforementioned processed object, and this process, and includes a tungsten element in the atmosphere of boron content gas after a short-time \*\*\*\* boron \*\* process and this process. Thereby, resistivity of a tungsten film is

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#### **CLAIMS**

# [Claim(s)]

[Claim 1] The membrane formation method of the tungsten film characterized by providing the following. The nucleus crystal-growth process of growing up the nuclear crystal of a tungsten into the bottom of existence of the membrane formation gas which faces in a vacuum processor forming a tungsten film on the front face of a processed object, and contains a tungsten element on the front face of the aforementioned processed object. After this process, it is a short-time \*\*\*\* boron \*\* process to the atmosphere of boron content gas about the aforementioned processed object. The tungsten membrane formation process which the aforementioned nuclear crystal is grown up and forms a tungsten film in the bottom of existence of the membrane formation gas containing a tungsten element after this process. [Claim 2] It is the membrane formation method of the tungsten film according to claim 1 characterized by the flow rate being 0.85% or more of abbreviation to the total gas total flow in the aforementioned

boron \*\* process, using hydrogen dilution diboron-hexahydride gas as the aforementioned boron content

[Claim 3] The aforementioned tungsten membrane formation process is the membrane formation method of the tungsten film according to claim 1 or 2 characterized by being the process which performs simultaneously embedding of the hole formed in the front face of the aforementioned processed object,

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# DETAILED DESCRIPTION

[Detailed Description of the Invention]

[The technical field to which invention belongs] this invention relates to the membrane formation method of the tungsten film which can improve specific resistance.

[Description of the Prior Art] Generally, in order to form a circuit pattern in the semiconductor wafer front face which is a processed object in the manufacturing process of a semiconductor integrated circuit, in order to embed the holes during wiring etc., or in order to perform these both simultaneously, making a metal or metallic compounds, such as W (tungsten), WSi (tungsten silicide), Ti (titanium), TiN (titanium night RAIDO), and TiSi (titanium silicide), deposit, and forming a thin film is performed. [0003] In the formation method of this kind of metal thin film, three methods (hydrogen), for example, H2 reduction, SiH4 reduction (silane), SiH2 Cl2 reduction (dichloro silane), etc. are known. SiH2 Cl2 It is the method of forming W and a WSi (tungsten silicide) film under the elevated temperature of about 600 degrees C, using a dichloro silane as a reducing gas, in order that reduction may form a circuit pattern. SiH4 Reduction is the method of forming W and a WSi film under the low temperature of about 350 degrees C of lows rather than previously, using a silane as a reducing gas, in order to form a circuit

[0004] Moreover, H2 Reduction is a method of using hydrogen as a reducing gas and making W film mainly depositing under the temperature of about 400-460 degrees C for stopgap on a wafer front face like the hole during wiring. In the above-mentioned case, all 6 (6 tungsten fluoride), for example, WF, are used. Here, explanation of the membrane formation method of the conventional tungsten film forms for example, the Ti/TiN film in the front face of a semiconductor wafer thinly as a barrier metal in advance of membrane formation of a tungsten film first. next -- as membrane formation gas -- WF6, SiH4, and H2, Ar and N2 etc. -- it introduces in a membrane formation chamber and the nuclear crystal of a tungsten is made to adhere and form in the front face of the above-mentioned barrier metal [0005] after [ next, ] once carrying out vacuum length of the inside of a membrane formation chamber to base \*\* and eliminating residual gas -- Ar, H2, and N2 Supply gas into a chamber and a pressure up is carried out to process \*\* for a short time. Furthermore, WF6 Gas is supplied by the predetermined flow

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rate and it is WF6. It is gas SiH4 It is H2 without using gas. A hydrogen reduction is carried out by gas, and a tungsten film is formed, for example, embedding of a hole and formation of a wiring layer are performed simultaneously.

[0006]

[Problem(s) to be Solved by the Invention] By the way, it is required that line breadth and the diameter of a hole should also be further made detailed according to this by the request of multilayering of a semiconductor integrated circuit, the further raise in detailed, and high integration. In this case, if a circuit pattern etc. turns minutely, although the part and resistance will rise, what was resistivity sufficient by the conventional design design needs to lower resistivity further by detailed-ization. However, it was difficult to obtain a tungsten film with which resistivity suits a design design small enough and new by the conventional membrane formation method of a tungsten film which was described above.

[0007] Then, it is Ar and N2 as the technique of solving the above-mentioned trouble in boron content gas (B-2 H6), for example, a diboron hexahydride, at the time of membrane formation of the tungsten film after adhesion formation of the nuclear crystal of a tungsten. With gas, addition introduction is carried out into a chamber and, thereby, the attempt which enlarges the diameter of tungsten crystal grain and lowers resistivity is performed. However, there was also a problem that nitrogen dilution diboron-hexahydride gas carried out a polymerization, for example, solidified within the pipe line in the middle of supply, and produced piping plugging etc. this invention is originated paying attention to the above troubles that this should be solved effectively. The purpose of this invention is to offer the membrane formation method of the tungsten film which can make resistivity small.

[Means for Solving the Problem] this invention person is after formation of a tungsten nucleus crystal, as a result of inquiring wholeheartedly about the membrane formation method of a tungsten film, and he used to result in this invention by acquiring the knowledge that the diameter of crystal grain can be enlarged at the time of subsequent membrane formation by carrying out boron-ized surface treatment of the semiconductor wafer by boron content gas, for example, a diboron hexahydride, just before actually forming a tungsten film. Invention specified to a claim 1 is faced forming a tungsten film on the front face of a processed object in a vacuum processor. The nucleus crystal-growth process of growing up the nuclear crystal of a tungsten into the bottom of existence of the membrane formation gas containing a tungsten element on the front face of the aforementioned processed object, After this process, the aforementioned processed object in the atmosphere of boron content gas A short-time \*\*\*\* boron \*\* process, It constitutes so that it may have the tungsten membrane formation process which the aforementioned nuclear crystal is grown up and forms a tungsten film in the bottom of existence of the membrane formation gas containing a tungsten element after this process.

[0009] Thus, it is, after growing up the nuclear crystal of a tungsten, and the crystal grain (grain) of a tungsten film becomes large at the time of subsequent film growth by carrying out boron surface treatment of the nuclear crystal of a tungsten by exposing a processed object to the atmosphere of boron content gas, just before actually forming a tungsten film, and it becomes possible to make resistivity small. In this case, when hydrogen dilution diboron-hexahydride gas is used 5% as the aforementioned boron content gas so that it may specify to a claim 2, this flow rate is considered as 0.85% or more of abbreviation to the total gas total flow. Thereby, resistivity can be made quite small.

[0010] As specified to a claim 3, the aforementioned tungsten membrane formation process is a process which performs simultaneously embedding of the hole formed in the front face of the aforementioned processed object, and wiring.

[0011]

[Embodiments of the Invention] Below, one example of the membrane formation method of the tungsten film concerning this invention is explained in full detail based on an accompanying drawing. <u>Drawing 1</u> is the outline block diagram showing the vacuum processor for enforcing the membrane formation method of the tungsten film of this invention. First, the vacuum processor for enforcing this invention method is explained. It has the processing container 4 fabricated by aluminum etc. in the shape of a

cylinder, and, as for this vacuum processor 2, the reflector 6 of the shape of a cylinder made to stand up from a processing container pars basilaris ossis occipitalis is formed in this processing container 4. On this reflector 6, the installation base 10 for laying the semiconductor wafer W is formed as a processed object through the L character-like attachment component 8 on the upper surface. This installation base 10 is constituted by aluminum compounds, such as a carbonaceous material with a thickness of about several mm and AlN.

[0012] The transparency aperture 12 which consists of a quartz etc. is airtightly formed in the processing container bottom just under this installation base 10, and as the transparency aperture 12 is surrounded in this lower part, the box-like heat chamber 14 is formed. In this heat chamber 14, two or more heat lamps 16 are attached in the rotation base 18 which serves also as a reflecting mirror, and rotate this rotation base 18 with a rotary motor 20. Therefore, the heat ray emitted from this heat lamp 16 can penetrate the transparency aperture 12, can irradiate the undersurface of the installation base 10, and can heat the wafer W on this now indirectly. And the exhaust port 22 is formed in the bottom periphery of a processing container, the flueway 24 connected to the vacuum pump which is not illustrated is connected to this exhaust port 22, and it has come to be able to carry out the vacuum length of the inside of the processing container 16. Moreover, the gate valve 26 opened and closed in case it carries out taking-out close [ of the wafer ] is formed in the side attachment wall of the processing container 4. [0013] on the other hand, the shower head section 28 which introduces a raw gas etc. into the processing container 4 prepares in the above-mentioned installation base 10 and the processing container ceiling section which counters -- having -- \*\*\*\* -- injection side 28A of this shower head section 28 -- many blows of gas -- a hole 30 is formed The gas supply system which supplies gas required for membrane formation processing etc. is connected to the gas inlet 32 of this shower head section 28. It is WF6 in order [ which is specifically depended on the boron content gas by which it is characterized / formation of the nuclear crystal of a tungsten, membrane formation of a tungsten film, and / of this invention / here ] to process by exposing. Gas, Ar gas, and SiH4 Gas and H2 Gas and N2 Gas and B-2 H6 Each source of gas of gas is connected. On both sides of the mass-flow controller 34 as a rate controller, and this, two opening-and-closing valves 36 and 38 are formed in piping of each source of gas, respectively, and control of flow of each gas and existence of supply can be chosen now as it.

[0014] Although the diboron hexahydride (B-2 H6) is used as the above-mentioned borane content gas, in order to prevent this polymerization solidification not using the diboron hexahydride of concentration 100%, the hydrogen dilution crimp run gas of 5% concentration which diluted concentration with hydrogen (H2) gas to 5% is used here. Moreover, the capacity of the processing container 4 used here is 3 1200cm of abbreviation. It is a grade, and the diameter of the installation base 10 is set as about 200mm, and can process the wafer of 8 inch size now.

[0015] Next, it explains, also referring to drawing 2 about this invention method performed using the equipment constituted as mentioned above. First, Wafer W is carried in in the processing container 4 by the conveyance arm which does not open and illustrate the gate valve 26 prepared in the side attachment wall of the processing container 4, and this wafer W is laid on the installation base 10. As shown in drawing 2 (A), the thin barrier metal 40 which consists of Ti/TiN is formed in the front face of this wafer W at the last process. This barrier metal 40 is formed also in the inside of the holes 42, such as a contact hole and a beer hall. Moreover, the path of a hole 42 is about 0.5-1.0 micrometers, and the aspect ratio of this hole 42 is one to about two. As for 44, a doped polysilicon film and 46 are insulator layers

[0016] next -- as the raw gas from each source of a raw gas -- WF6, Ar, SiH4 and H2, and N2 -- the shower head section 28 -- every [ the specified quantity ] -- supplying -- mixing -- this -- a blow of gas at the bottom -- it supplies equally [abbreviation] into the processing container 40 from a hole 30 Here, it is B-2 H6. Gas is not supplied. By being able to come, simultaneously carrying out the suction exhaust air of the interior atmosphere of exhaust-port 22 shell, the inside of the processing container 4 is set to a predetermined degree of vacuum, for example, the value of about 4 Torrs, and the heat lamp 16 in a heat chamber 14 is rotated, a \*\*\*\* drive is carried out, and heat energy is emitted.

[0017] After the emitted heat ray penetrates the transparency aperture 12, it irradiates the rear face of the

installation base 10, and heats this. The wafer W which this installation base 10 is quickly heated as mentioned above from about several mm and a very thin thing, therefore has been laid on this can be quickly heated to predetermined temperature. The process temperature at this time is about 460 degrees C. The supplied mixed gas is WF6, as a predetermined chemical reaction is produced and it is shown in drawing 2 (B) here. It will be returned, adhesion formation of the nuclear crystal 48 of a tungsten will be carried out on the front face of the barrier metal 40, and a nucleus crystal-growth process is performed. This nucleus crystal-growth process is performed about 30 seconds, for example, and forms the nuclear crystal layer whose thickness is about 30nm.

[0018] Thus, if a nucleus crystal-growth process is ended next, it will shift to a boron \*\* process. First, supply of reactant gas is stopped, vacuum length is carried out to base about \*\*, for example, 10 to 3 Torrs, at once, and it is B-2 H6 further. Supplying the predetermined gas which makes gas the start and carrying out a pressure up to about 80 Torrs, as shown in drawing 2 (C), a boron \*\* process is performed. A distributed gas kind here is Ar gas and H2. Gas and B-2 H6 It is gas and each capacity is 4000sccm, 1800sccm, and 100sccm(s) (5% concentration). Here, it is WF6. Gas, SiH4 gas, and N2 Supply of gas is not carried out. Thereby, it is exposed to boron and the tungsten nucleus crystal 48 is B-2 H6. A boron front face is formed by gas. It becomes possible to enlarge particle size of a nuclear crystal by this, so that it may mention later. This boron \*\* process is performed about 28 seconds, for example. In addition, the process temperature at this time is about 460 degrees C, and is the same as a last process.

[0019] Thus, if a boron \*\* process is ended next, it will shift to an actual tungsten membrane formation process. First, WF6 Gas, Ar gas, and H2 Gas and N2 100sccm supply of the gas is carried out 750 sccm 900 sccm 80 sccms, respectively, and actual membrane formation of a tungsten film is performed. Here, they are SiH4 gas and B-2 H6. Supply of gas stops. A process pressure and process temperature are the same as a last process respectively, and are 80Torr and 460 degrees C. The tungsten film 50 for wiring will be formed in a front face at the same time a hole 42 (refer to drawing 2 (A)) is embedded by this, as shown in drawing 2 (D). The processing time at this time is about 98 seconds, and forms the tungsten film 50 of 800nm thickness on the whole.

[0020] Thus, particle size of the tungsten nucleus crystal (grain) which grows in a back process can be enlarged by incorporating a boron \*\* process, exposing a tungsten nucleus crystal to a diboron hexahydride, and forming a boron front face between a nucleus crystal-growth process and the tungsten membrane formation process which actually forms a tungsten film. For this reason, the crystal structure of the formed tungsten film 50 becomes a thing near a bulk crystal, and can make resistivity small. [0021] B-2 H6 Although the resistivity (1500A conversion) of the tungsten film by the conventional method was about 12.2 microomegacm as a result of comparing with this invention method the conventional membrane formation method of not using gas, the resistivity (1500A conversion) of the tungsten film by this invention method is about 8.5 microomegacm, and that it is sharply improvable made resistivity clear.

[0022] <u>Drawing 3</u> is the electron microscope photograph of the cross section of the hole embedding portion by the tungsten film which formed membranes by the above-mentioned method, and it becomes clear that the particle size of the tungsten nucleus crystal of this invention method shown in <u>drawing 3</u> (B) is large clearly as compared with the conventional method shown in <u>drawing 3</u> (A), and it is in the state near a bulk crystal. Moreover, in the case of this invention method, about the embedding of a hole 42, the problem was not produced at all, but it was in the good embedding state like the conventional method.

[0023] Furthermore, by this invention method, it sets at the above-mentioned boron \*\* process, and is B-2 H6 of 5% concentration of hydrogen dilution. Although 100sccm addition of the gas is carried out, resistivity will not become so small, if it is desirable that this quantity of gas flow is 0.85% (\*\*50x100/(4000+1800+50)) of more than abbreviation to 50 or more sccms of abbreviation of gas total, i.e., the total amount, and it is smaller than this. This point is explained with reference to drawing 4. Drawing 4 is B-2 H6, in order to show the above-mentioned result. It is the graph which shows the relation between the flow rate of gas (5% concentration), and resistivity (1800A conversion). In addition, it is Ar quantity

of gas flow and H2 as mentioned above. The quantity of gas flow is fixed to 4000sccm(s) and 1800sccm (s), respectively.

[0024] It is B-2 H6 so that clearly from this graph. When there are few flow rates of gas (5% concentration of hydrogen dilution) than 50sccm(s) Although the resistivity of a tungsten film is large and more desirable than 11.3microomegacm, if set to 50 or more sccms Resistivity becomes smaller than 11microomegacm, therefore is B-2 H6. That it is good setting it as 50 or more (it being 0.85% or more of abbreviation to the total gas total flow) sccms makes clear the flow rate of gas (5% concentration of hydrogen dilution) gas.

[0025] Moreover, with this invention method, it is B-2 H6. Since the dilution gas which diluted this gas to concentration 5% with hydrogen gas as gas is used It is B-2 H6 like the conventional method. It differs from the case where the gas which diluted gas with nitrogen gas or argon gas is used, and is B-2 H6. Gas is the inside of the source container of gas, and B-2 H6. It can also be prevented that do not carry out a polymerization within the charging-line system of gas, and the pipe line carries out blinding with a polymerization solid. Drawing 5 is also referred to and explained about this point. Drawing 5 is N2 as dilution gas. The case where gas (the conventional method) is used, and H2 It is the graph which shows concentration change of the diboron hexahydride (B-2 H6) at the time of using gas (this invention method). It is N2 so that clearly from this graph. Since the concentration of a diboron hexahydride is falling so that lapsed days increase in gas dilution, it becomes clear that the diboron hexahydride has caused the polymerization. On the other hand, H2 used by this invention method In gas dilution, regardless of lapsed days, the concentration of a crimp run is carrying out abbreviation regularity, the polymerization is not caused, and it becomes clear in it that it is in a good state. This is N2. When gas is used for dilution base gas, it is B-2 H6. It is thought that it is because it takes and becomes unstable in

[0026] In addition, the quantity of gas flow in the above-mentioned example, process temperature, and the process pressure of not passing an example only having been shown and not being limited to them are natural. Moreover, B-2 H6 of 5% concentration according to hydrogen dilution at this example Although gas is used, if the concentration of this dilution changes, of course, the threshold value of each amount of supply mentioned above also changes in proportion to it. furthermore, the boron content gas to be used is also limited to a diboron hexahydride -- not having -- other boranes, such as a tetraborane and a pentaborane, and BCl3 etc. -- it not only can use, but wafer size can use the thing of other sizes Furthermore, as a processed object, not only a semiconductor wafer but a glass substrate, a LCD substrate, etc. can be used. [0027]

[Effect of the Invention] As explained above, according to the membrane formation method of the tungsten film of this invention, the operation effect which was excellent as follows can be demonstrated. It faces forming a tungsten film on the front face of a processed object, and between a nucleus crystalgrowth process and the tungsten membrane formation process which actually forms membranes, since it was made to perform the boron \*\* process which exposes a processed object to boron content gas, particle size of tungsten crystal grain (grain) can be enlarged, and this resistivity can be made small.

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# **DESCRIPTION OF DRAWINGS**

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram showing the vacuum processor for enforcing the membrane formation method of the tungsten film of this invention.

[Drawing 2] It is process drawing for explaining the membrane formation method of this invention.

[Drawing 3] It is the electron microscope photograph of the cross section of the hole embedding portion by the tungsten film.

[Drawing 4] B-2 H6 It is the graph which shows the relation between the flow rate of gas (5% concentration), and resistivity.

[Drawing 5] It is N2 as dilution gas. The case where gas (the conventional method) is used, and H2 It is the graph which shows concentration change of the diboron hexahydride (B-2 H6) at the time of using gas (this invention method).

[Description of Notations]

- 2 Vacuum Processor
- 4 Processing Container
- 10 Installation Base
- 12 Transparency Aperture
- 16 Heat Lamp
- 28 Shower Head Section
- 40 Barrier Metal
- 42 Hole
- 44 Doped Polysilicon Film
- 46 Insulator Layer
- 48 Nuclear Crystal of Tungsten
- 50 Tungsten Film
- W Semiconductor wafer (processed object)

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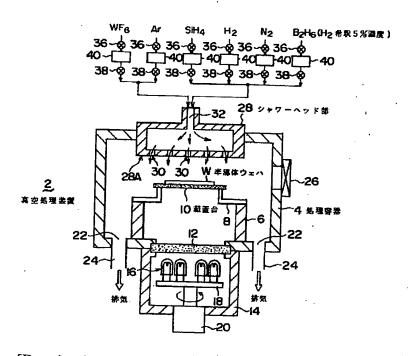
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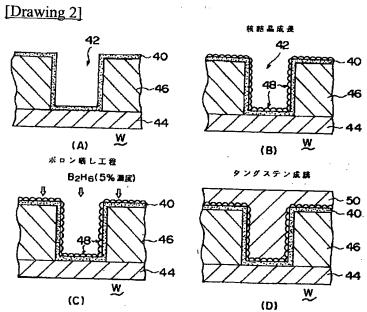
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#### DRAWINGS

# [Drawing 1]





[Drawing 3]

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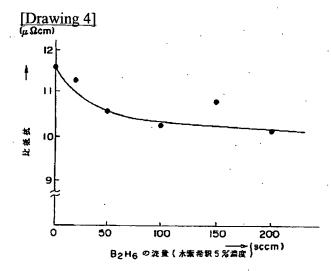
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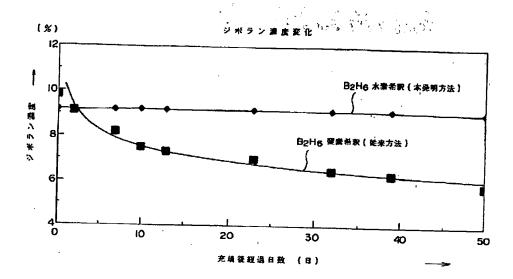


12. 2 μΩ c m (A)

8. 5 μ Ω c m(B)



[Drawing 5]



[Translation done.]